

Low Cost Carbon Fiber Technology Development for Carbon Fiber Composite Applications

APRIL 2012

FTA Report No. 0011
Federal Transit Administration

PREPARED BY

Ahmad D. Vakili
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The University of Tennessee
Space Institute



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Metric Conversion Table

SYMBOL	WHEN YOU KNOW	MULTIPLY BY	TO FIND	SYMBOL
LENGTH				
in	inches	25.4	millimeters	mm
ft	feet	0.305	meters	m
yd	yards	0.914	meters	m
mi	miles	1.61	kilometers	km
VOLUME				
fl oz	fluid ounces	29.57	milliliters	mL
gal	gallons	3.785	liters	L
ft³	cubic feet	0.028	cubic meters	m ³
yd³	cubic yards	0.765	cubic meters	m ³
NOTE: volumes greater than 1000 L shall be shown in m ³				
MASS				
oz	ounces	28.35	grams	g
lb	pounds	0.454	kilograms	kg
T	short tons (2000 lb)	0.907	megagrams (or "metric ton")	Mg (or "t")
TEMPERATURE (exact degrees)				
°F	Fahrenheit	5 (F-32)/9 or (F-32)/1.8	Celsius	°C

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13. ABSTRACT The objective of this project was to further develop low cost carbon fiber for a variety of potential applications. Manufacturing feasibility of low cost carbon fibers/composites has been demonstrated. A number of technologies that are currently using other synthetic fibers may use high strength lightweight and low cost carbon fibers to reduce weight and improve performance. New applications that are in the nation's interest may also be developed. Production of lightweight automobiles, buses, trains, and ships, including lightweight select body panels, load bearing structures, and other transportation system components, could result in major weight savings and result in significant reduction in the energy used.			
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EXECUTIVE SUMMARY

The objective of this project is to further develop low-cost carbon fiber for a variety of commercial applications. A number of technologies that are currently using other synthetic fibers can use high-strength, lightweight, and low-cost carbon fibers to reduce weight, improve performance, and generate new applications that are in the nation's interest. Low-cost carbon fiber will be in a position to provide enormous advantages to a number of technologies for current and future everyday life, including a number of advanced technology applications that currently are not commercially feasible. Lightweight automobiles, buses, trains, aircraft, ships, and applications including lightweight body panels and load-bearing structures and many other transportation systems components will result in tremendous weight savings and would result in major saving in the energy used for such purposes.

During the past many years, scientists and engineers in various companies and at a number of universities have developed nearly all the process technologies for a pitch-based carbon fiber manufacturing process. The technology has been developed and demonstrated in a spin research lab that was developed, in part, with the help of Professor Ahmad Vakili, this project's principal investigator.

The use of pitch precursor has the promise to significantly reduce the final cost for carbon fiber production. The University of Tennessee Space Institute (UTSI) is in a unique position to continue pitch-based carbon fiber (PBCF) research and development (R&D) to improve certain technology areas and to enable a viable low-cost commercial process for carbon fiber production from pitch. Other related technology areas such as rechargeable batteries, fuel-cell electrodes, lightweight paneling, advanced lightweight general structures, and fiber-reinforced concrete and asphalt are just a few examples.

Low-cost carbon fiber is a national goal, established to accomplish a number of technological breakthroughs. Major savings in energy consumption would be possible with the use of lightweight high-strength fibers in the automobile industry.

UTSI formed a major R&D program around (pitch-based) carbon fibers production and advanced carbon fiber-based material applications. These R&D efforts include forming a consortium of interested universities, government labs, and industrial partners to work collaboratively and to accomplish the goal of accomplishing low-cost carbon fiber production technology in a timely manner. The consortium will possess unique lab facilities to perform necessary R&D work in cooperation with partners. UTSI and the consortium members will also be collaborating on composite materials development and applications that would raise the demand and, therefore, the support for large-scale commercial production of low-cost carbon fibers.

Success criteria include development of commercially-viable processes and methodologies for low-cost carbon fiber production and fiber applications in industrial products.

SECTION 1

Introduction

In December 2004, The University of Tennessee Space Institute (UTSI) received state-of-the-art lab equipment and technologies pertinent to a low-cost, pitch-based carbon fiber technology program from ConocoPhillips. The University developed a plan to continue the development of the low-cost carbon fiber production and application technologies at UTSI. Prior to the University receiving this technology, pitch-based carbon fiber development efforts have been in research and development for more than 25 years by a number of different companies, including Union Carbide, Exxon, DuPont and ConocoPhillips.

The objective of this program is to develop production technologies for low-cost carbon fiber for a variety of commercial applications. A number of technologies that are currently using synthetic fibers can use high-strength, lightweight, and low-cost carbon fibers to reduce weight, improve performance, and generate new applications that are in demand. Low-cost carbon fiber could provide enormous advantages to technologies for future everyday life, including advanced technology applications that are not commercially-feasible at higher carbon fiber prices. Low-cost carbon fiber (from pitch) is a national goal established to accomplish a number of technological breakthroughs. Huge savings in energy consumption would be possible with the use of lightweight, high-strength structures and body panels in the automobile industry and will lead to improvements in a number of other technology areas.

Implementation of the low-cost carbon fiber technology program was established and made possible at UTSI with partial funding from the Federal Transit Administration (FTA) under the research program titled “Low Cost Carbon Fiber Technology for Carbon Fiber Composite Applications.” The major goals of the research program at UTSI are to produce low-cost carbon fibers and develop carbon-based material technologies to meet existing and future needs of FTA and other funding organizations for high-performance carbon fibers. This report is the final technical report of this phase of the study to inform the funding agency and contract managers and others of the progress made during the period of performance of this program to date.

The main goals of this research program at UTSI are 1) to produce low-cost carbon fibers and 2) to develop specific carbon-based material technologies to meet current and future high-performance, fiber-reinforced composite needs of FTA and other organizations. UTSI has been carrying out the relevant research programs since it received carbon fiber spinning technologies and accessories as a donation from ConocoPhillips. Under this U.S. DOT-sponsored program, significant progress has been made in the continued development and refinement of low-cost carbon fiber production and composite application technologies.

The task at hand is a major multidisciplinary effort and will need to be continued to reach successful completion and for continuous improvements. A dedicated webpage of the UTSI carbon fiber program can be found at <http://www.utsi.edu/research/carbonfiber/index.html>; the content of this site is regularly and continuously updated with the latest major progress and accomplishments.

SECTION
2

Production and Characterization of Carbon Fibers

Research Labs and Equipment for Carbon Fibers

Significant effort has been made to establish research labs at UTSI for carbon fiber production, processing, and characterization. The process of bringing the UTSI Spin Lab online was systematic but time-consuming, as certain components in the lab involved precision instrumentation. Initial efforts comprised installing and testing spin lab equipment and procurement of a number of special furnaces for heat treatment of pitch fibers, including drying, stabilization, and carbonization.

UTSI initiated and completed assembly of different spin system components and equipped the lab with basic support utilities. Since the equipment received had little installation documentation, the assembly included identification and verification of utilities needs, and controls; connection of the electrical system; and determination of safe control and operations procedures for individual subsystem components and the working of all subsystems cumulatively, including documenting their installation and developing operations manuals.

Figure 2-1
UTSI Spin Lab: close view of spin tower, control panel, and fiber collection platform with secondary gas heater (white duct) in foreground



The spin system is composed of a number of highly-specialized and sophisticated components and has a number of built-in interlocking devices that had to be individually tested and functionally verified. Furthermore, the operation of the various components for ideal spinning of pitch fiber needed to be well understood. The UTSI Spin Lab, including different components and systems of the UTSI carbon fiber spin facility, is shown in Figure 2-1.

Another important aspect of the carbon fiber process is heat treatment or thermal processing. Heat treatment is a key step in carbon fiber production. Various specialty furnaces were examined from different sources, including the inventory of UTSI research equipment. Three furnaces, as shown in Figure 2-2, were obtained and set up for drying, oxidative stabilization and pre-carbonization, and high-temperature carbonization and graphitization. A retort chamber delivered as part of the original equipment was reconfigured for more uniform heating under the oxidation atmosphere.

Figure 2-2

Furnaces used for carbon fiber thermal processes: drying and stabilization (left), pre-carbonization (center), and high-temperature carbonization and graphitization furnaces (right)

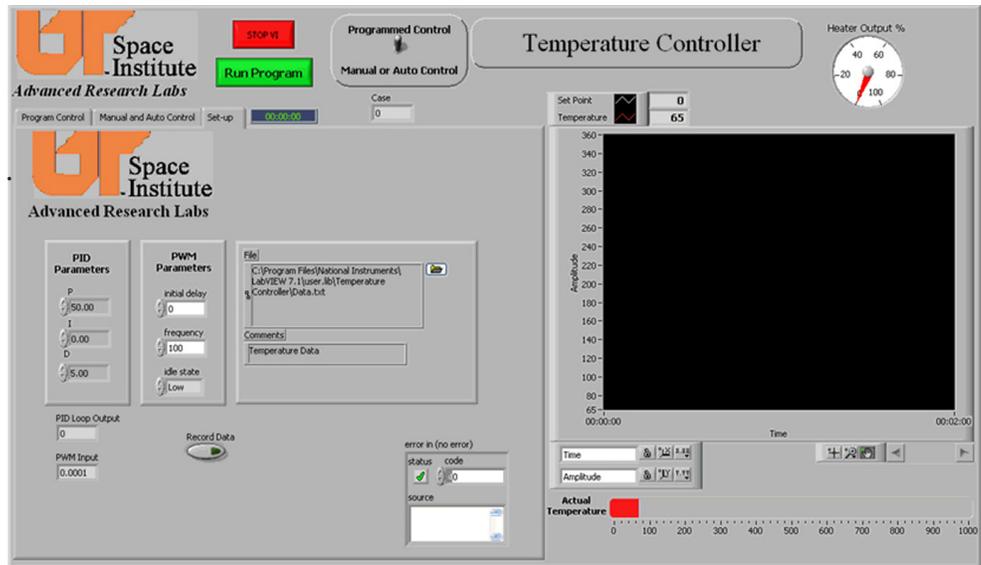


The pre-carbonization furnace can be operated at temperatures up to 1200°C. During pre-carbonization, stabilized fibers are heated in an inert atmosphere, and volatiles, along with decomposition gases—for example, H₂O, CO₂, CO, and H₂, are removed. A high-temperature furnace can be operated up to ~ 2400°C for carbonization and graphitization. Unlike PAN fibers, pitch-based carbon fibers tend to attain higher tensile strengths and higher thermal and electrical conductivity at higher processing temperatures.

The heating profiles are designed to balance several conflicting factors, e.g., slow enough to maintain the rate of mass transfer to avoid surface irregularities while completing the overall processing at the shortest possible time. A Labview-based controller (Figure 2-3) was implemented to automate the process. This also allows the operator to set the heat treatment steps remotely, i.e., the operator does not need to be physically present near the furnace during the heat treatment.

The user interface of the LabView Virtual Instrument (VI) was designed as generically as possible to allow wide applications to other furnaces in this project.

Figure 2-3
*LabView-based
temperature control
interface panel*



Carbon Fiber Production Processes

Pitch-based carbon fibers are produced from a series of processing steps, principally consisting of precursor preparation, fiber spinning, oxidative stabilization, carbonization, and sometimes graphitization. One of the special features of the pitch-based carbon fiber technology at UTSI is that the precursor pitch is solvated mesophase pitch, which contains about 10 to 20 wt% of spin solvent, which enables melt blow spinning at a high production rate. The use of spin solvent also requires an additional drying step once the fiber spinning is completed.

Precursor Pitch

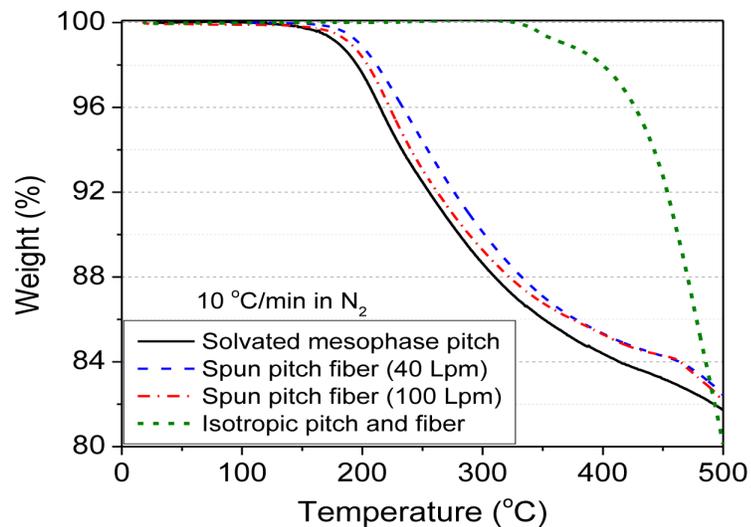
The fiber precursor employed at UTSI is the solvated mesophase pitch produced from a discontinued commercial plant by ConocoPhillips. This precursor material is different from conventional pitch used for the commercial products of pitch-based carbon fibers. It contains thermally some processed pitch oils as a spin solvent, which has a fundamental influence on the mesophase pitch property, fiber spinning operation, and processing of spun pitch fibers. The advantages of solvated pitch [1, 2] are:

- It adequately uses a higher fraction of high molecular raw pitch materials.
- It makes the pitch more spinnable at lower temperatures with a high production rate.
- Its high molecular weight makes the spun pitch fiber easier to stabilization.

However, the solvents inside the pitch after spinning must be removed prior to carbonization, because it is likely to introduce more voids and defects into the resulting carbon fiber and to reduce its mechanical properties. Experimental efforts have been initiated to look into the solvated pitch to understand the thermal behavior of solvents.

TGA analyses in N_2 comparing solvated mesophase pitch with isotropic pitch (no solvents) are shown in Figure 2-4. Without solvents, isotropic pitch shows an onset point of weight loss at $\sim 335^\circ\text{C}$. In contrast, solvated mesophase pitch and its fibers start weight loss at $\sim 150^\circ\text{C}$. There is ~ 14 wt% solvent removal for solvated mesophase pitch and ~ 13 wt% for its spun fibers at 350°C .

Figure 2-4
TGA analyses in N_2
comparing solvated
mesophase pitch
with isotropic pitch



Fiber Spinning

Pitch fibers have been successfully produced in the UTSI Spin Lab. Continuous and uninterrupted spinning for a certain period of time is one measure of success. Production of uniform quality fiber with the desired diameter, tensile, and modulus collected either in the form of a nonwoven mat or wound on spools is the necessary component of the spinning success. Figure 2-5 shows the operation of UTSI fiber spinning facility (left) and the samples of spun pitch fiber or “as-spun” or “green fibers” (right).

Figure 2-5
Fiber spinning
facility (left) and
spun fibers (right)



The final fiber diameter is achieved through attenuation of the molten pitch near the die tip and is primarily influenced by the two parameters: 1) the softening temperature of the mesophase pitch as it exits the capillary (die tip), and 2) the flow conditions of the primary and secondary gas flow that exert a specific tension on the fiber near the capillary exit. The spin temperature is usually about 40–50°C higher than the softening temperature. The region very close to the orifice exit is extremely crucial in the fiber formation process. Solvent and pitch volatiles start to escape from the fiber, moving the softening temperature progressively higher and impeding the attenuation of green fibers. The fiber diameter was controlled by adjusting the air-blowing speeds. The average diameter of the resulting carbon fiber was about 10 microns for the higher flow-rate condition, very close to the target range for carbon fibers made from PAN and pitch. TGA measurements were also made on green fibers (as-spun). Green fibers show a behavior very similar to pitch. That means that the process of spinning has not significantly reduced the amount of solvent present, as shown in Figure 2-4.

Sufficient amounts of green fibers were produced to support stabilization- and carbonization-related experiments.

Drying and Stabilization

To make pitch fiber infusible at higher carbonization temperatures, dry (removal of solvents) and oxidation (introduction of oxygen-containing groups) stabilization processes have been performed to stabilize the fiber prior to carbonization process. Stabilization in flowing air is believed to be the most economical process in the manufacturing of carbon fibers [3]. Usually, stabilization is carried out at temperatures slightly above 300°C in a specially-modified furnace chamber with a reaction volume of about 3 cubic feet. Oxidative stabilization is an important step to avoid softening and melting of carbon fibers at higher processing temperatures. The step could take a long time, sometimes several hours, and it is a time-consuming step in the continuous processing of fibers. For example, the fibers may be spun continuously at about 80 to 100 mph, and an impractical length of equipment would be required if the thermal processing is operated in a continuous fashion. In other words, fast processing time is essential for industrial processing. Key parameters involved in the oxidation process include 1) final oxidation temperature, 2) rate of heating and total time required for oxidation, 3) softening point of mesophase pitch and spun fiber, and 4) concentration of oxidant. Our primary objective is to minimize the time and temperatures required for oxidation.

Solvents in the pitch fiber can be effectively removed by heating the fiber in an inert gas, as shown in Figure 2-4. Without oxidative stabilization, dried fiber would melt and lose its fiber form during high-temperature treatment. For simultaneous drying and oxidation in air, the weight loss due to the removal of solvents and weight gain due to oxidation were strongly affected by heating rates. The fast heating rate resulting in more weight loss suggests that the removal of solvents is controlled by temperature, i.e., the dry process is temperature-dependent. In contrast, a very

slow heating rate resulting in more weight gain suggests that oxidation reaction is mainly controlled by time, i.e., the oxidative stabilization process is time-dependent.

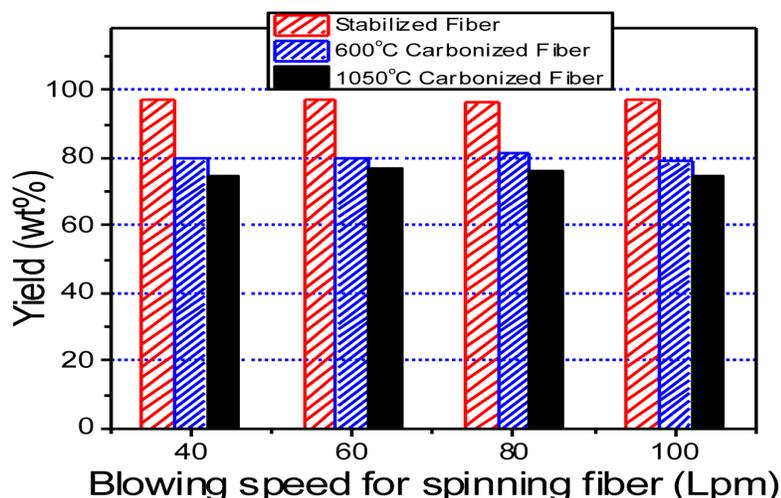
To effectively remove solvents and reduce oxidative stabilization time, separate dry and oxidation processes have been performed in the lab. Solvents were first removed in flowing N_2 , and then the dried fiber was oxidized in air. It was found that the dried fiber can be stabilized (retain fiber form) efficiently with a very short (2 mins) oxidation. Moreover, short-time (2–10 mins) oxidation contributes a higher carbon yield to the resultant carbon fiber. Moisture can be adsorbed onto the stabilized fibers due to the formation of polar, oxygen-containing groups. The moisture uptake increases proportionally with oxidation time. The prepared carbon fibers show increased (50–70%) tensile strength and modulus, as compared to carbon fiber prepared with a simultaneous dry and oxidation process. The optimal oxidation time is 30 to 60 min for thick fiber (40 Lpm) and only 2 min for thin fiber (100 Lpm).

Carbonization

After drying and stabilization, pitch fibers were carbonized up to $1050^\circ C$ in inert gas atmosphere to generate a sufficient amount of carbon fiber samples for various evaluations and different composite fabrications. More than 50 batches of carbonization runs have been carried out to date. Carbonization was conducted with the process temperature ramped up to $1050^\circ C$ for most experiments. The structure and properties of these carbon fibers have been characterized by various methods, as described in the following sections.

Four pitch fibers spun from different blow speeds were dried and oxidized in air and then carbonized in N_2 in some conditions. The yield of fibers was calculated from the changes in weight prior to and after thermal treatments, and the results are shown in Figure 2-6. Based on the original weight of pitch fibers, the resulting carbon fibers show a high carbon yield at ~75 wt% or even higher at ~86 wt% if disregarding the 13 wt% solvents in the original pitch fibers.

Figure 2-6
Yields of fibers after stabilization and carbonization at lower ($600^\circ C$) and higher ($1050^\circ C$) temperatures



To obtain higher strength and more balanced modulus, carbonization with high temperature is required. A furnace with graphite heating elements has been obtained and modified to accomplish this objective. Some high temperature carbonization was conducted up to 1550°C. Unfortunately, only a small amount of fiber can be produced due to its small effective volume. Carbon fibers prepared with a lower carbonization temperature of 1050°C show average tensile strength and modulus of 500–1100 Mpa and 70–110 Gpa, respectively. When the carbonization temperature increases to 1500°C, the strength and modulus can be up to 2.5 Gpa and 200 Gpa, respectively.

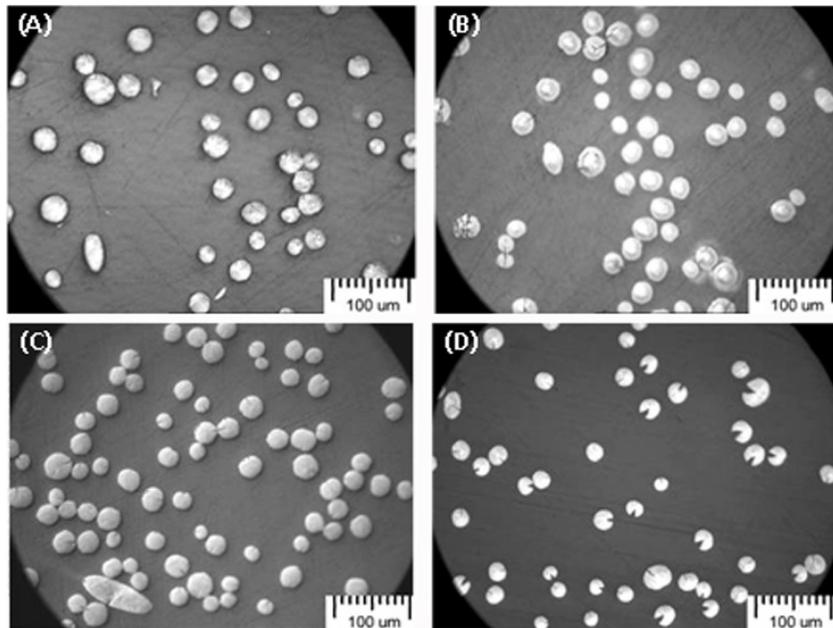
Structural Characterization of Fiber Products

The structure of carbon fibers is very important from microscopic to nano-scales in understanding the properties of fiber products and processing-related issues to improve the fiber quality and the performance of their composites. Comparing the conventional PAN and other pitch-based carbon fibers, substantial differences in their properties at the macroscopic, microscopic, and nanometer levels are expected. Differences are mainly due to the different precursors, special fiber spinning, and fiber processing methods employed.

Optical Microscopy

The fiber samples, including pitch fibers, stabilized fibers, and carbonized fibers, were mounted in epoxy resin and polished carefully. The transverse and longitudinal sections of each fiber were investigated using an optical microscope with a reflected light. As the graphene layer planes of crystallites in mesophase pitch

Figure 2-7
Optical microscope images showing the cross-sectional structures of (A) pitch (40 Lpm), (B) oxidized pitch, (C) 600°C carbonized, and (D) 1050°C carbonized fibers



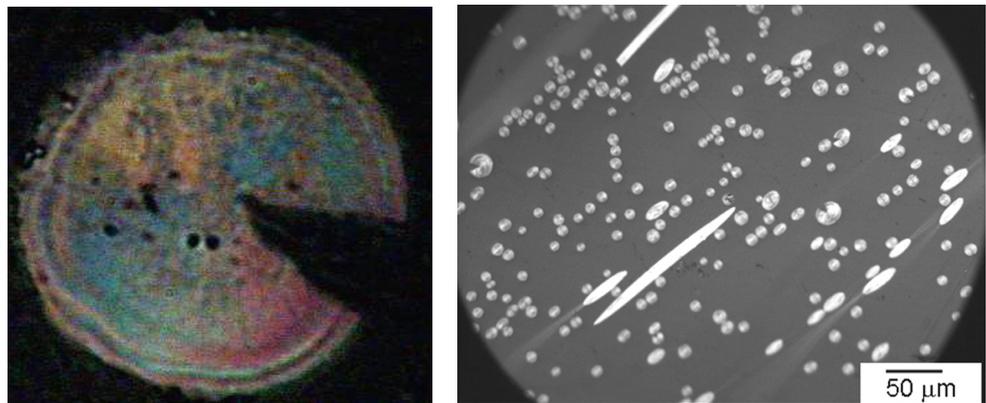
and graphite are optically anisotropic, the orientation of these aggregates within the fibers can be determined using polarized light. The optical micrographs of pitch fiber, stabilized green fiber, and 1050°C carbonized fiber are shown in Figure 2-7.

Nothing special was found in pitch fibers, except that the fiber diameter observed decreased with increasing blowing speed from 40 to 100 Lpm. After stabilization, sheath-core structures were observed in larger-diameter (40 Lpm) stabilized fibers, as shown in Figure 2-7 (B). However, no such structure was found in small-diameter (100 Lpm) stabilized fiber. Sheath is believed to be composed of well-stabilized, cross-linked, and relatively hard material, while core is composed of less-stabilized and relatively soft material [4]. When the fiber embedded in epoxy resin was polished, the fiber cross-sectional surface may not be flat due to the different wear properties of sheath and core materials. The center (core) of the fiber is lower than the edge (sheath), which is one explanation for a two-phase structure observed under the optical microscope. This result suggests that the stabilization of the pitch fiber is controlled by the diffusion of oxidation from the outside layer to the internal core [5]. Thus, small diameter fiber is easily stabilized uniformly, but larger diameter fiber may stabilize gradually, resulting in sheath-core structure.

Carbon fibers with a larger diameter presented a radial crack structure or a “Pac-Man structure,” as shown in Figure 2-7 (D) and Figure 2-8 (left). It was also found that the Pac-Man structures start to reveal themselves starting from 600°C and become distinctly noticeable at 700°C. From 800°C and up, the Pac-Man structures can be observed in almost every fiber, with the angle of the Pac-Man mouth being the greatest at 1050°C. For the small-diameter (100 Lpm) stabilized fiber, a sheath-core structure was not observed. As a result, the Pac-Man structure was not observed in the most carbonized fibers with a small diameter, as illustrated in Figure 2-8 (right).

Crack formation in mesophase pitch-based carbon fibers have been investigated [6-8] on melt spun fibers. It was found that the spinning conditions, such as

Figure 2-8
Optical microscope images showing (left) Pac-Man structure in a larger diameter carbon fiber, (right) cross-sectional structures of small-diameter (100 Lpm) carbon fibers

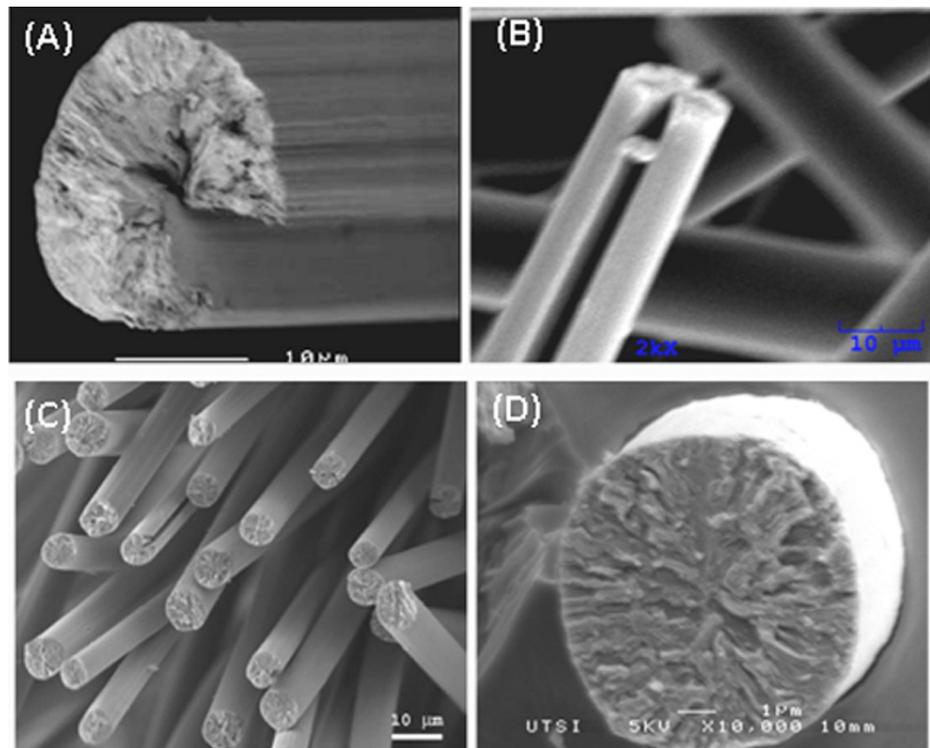


spinning temperature, L/D of nozzle dimension, diameter and wall material of the spinning nozzle, and the kind of mesophase pitch, influence crack formation [7-10]. However, for the solvated mesophase pitch fiber spun with melt-blowing techniques involved in this study, the larger diameter and sheath-core structure formed on the stabilized fiber could be related to the formation of the Pac-Man structure of the resulting carbon fiber. A typical Pac-Man structure in larger diameter carbon fibers is shown in Figure 2-8 (left). A crack (fiber with wedge), radial transverse microstructure, a thin layer of skin, and voids or pores are observed on the fiber cross-section.

Scanning Electron Microscopy (SEM)

The structure of various fibers was also investigated using SEM. As observed by optical microscopy, some fibers had a radial crack propagating along the fiber axis. Additionally, ridge-like features were observed in the outer surfaces. Typical SEM of the fiber carbonized 1050°C are shown in Figure 2-9 (A–B) at different magnifications. In the literature, the presence of such cracks has been attributed to the radial orientation of the crystal structures of the mesophase pitch. To eliminate such cracks, suggestions have been made to introduce some form of randomness into the pitch prior to spinning. This can be accomplished possibly by introducing turbulence upstream of the capillary exit. The ridges along the fiber length are somewhat more complex, probably due to release of spin solvents in the precursor pitch.

Figure 2-9
SEM images showing (A) and (B), larger-diameter carbon fiber with Pac-Man crack along the fiber axis, (C) and (D), smaller-diameter carbon fibers

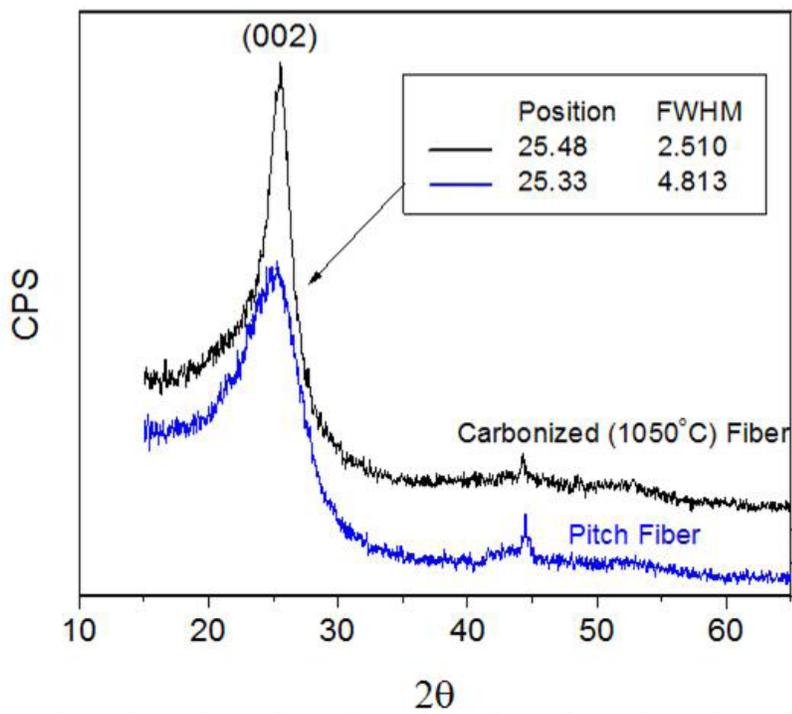


Micrographs of the most common fibers carbonized at 1050°C are shown in Figure 2-9 (C–D), revealing the general structural features of the carbon fibers produced at UTSI. These fibers have a round cross-section, and there are tracks or ridges running on the outer surfaces along the fiber length. The SEM micrograph of a carbon fiber in Figure 2-9 (D) contains detailed structure in terms of principal arrangements of graphene staking across the fiber surfaces. In this case, the graphene layers were folded to some extent but oriented generally in radial directions. These so-called folded radial structures are considered very desirable for mechanical strength and modulus. Such a structure is quite consistent with the observation by optical microscopy indicated above.

X-ray Diffraction

The microcrystalline structures of solvated mesophase pitch fiber and the resulting carbon fiber were characterized with an x-ray diffractometer. Both pitch fiber and carbon fiber display a main diffraction peak at $2\theta = 25^\circ$ and a small peak at $2\theta = 45^\circ$, as shown in Figure 2-10. As compared with mesophase pitch, the 1050°C carbonized fiber possesses a higher and sharper (narrower FWHM) peak with a somewhat higher position at a 2θ angle. According to Bragg's law and Scherer's equation used in carbon fiber research [11], the microcrystalline size (Lc) increased and the d-spacing (d002) decreased as the mesophase pitch was converted to carbon fiber at 1050°C.

Figure 2-10
X-ray diffraction patterns of solvated mesophase pitch fiber and the resulting carbon fiber

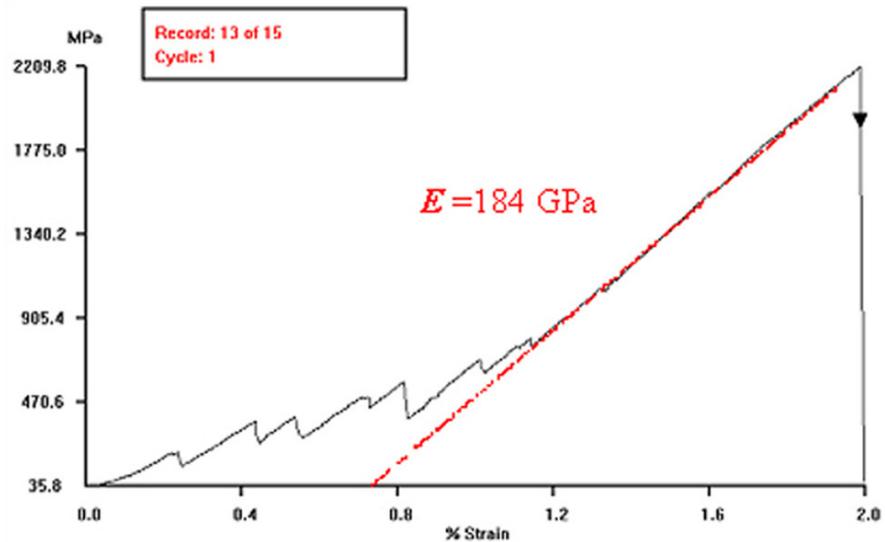


Single Filament Testing

Carbon fiber diameter and tensile properties (Figure 2-11) have been continuously evaluated using a single filament analyzer. Individual fiber filaments were carefully mounted on special sample support mounts before their diameters were measured by a laser micrometer. Fiber length used for these tests was 10 mm. The fiber analyzer instrument, an FDAS765 by Diastron Limited, is a high-resolution dimensional measurement system, with a force resolution of 0.005 grams and a positional repeatability of 0.1 microns.

Figure 2-11

Elongation of a single filament carbon fiber vs. applied tension



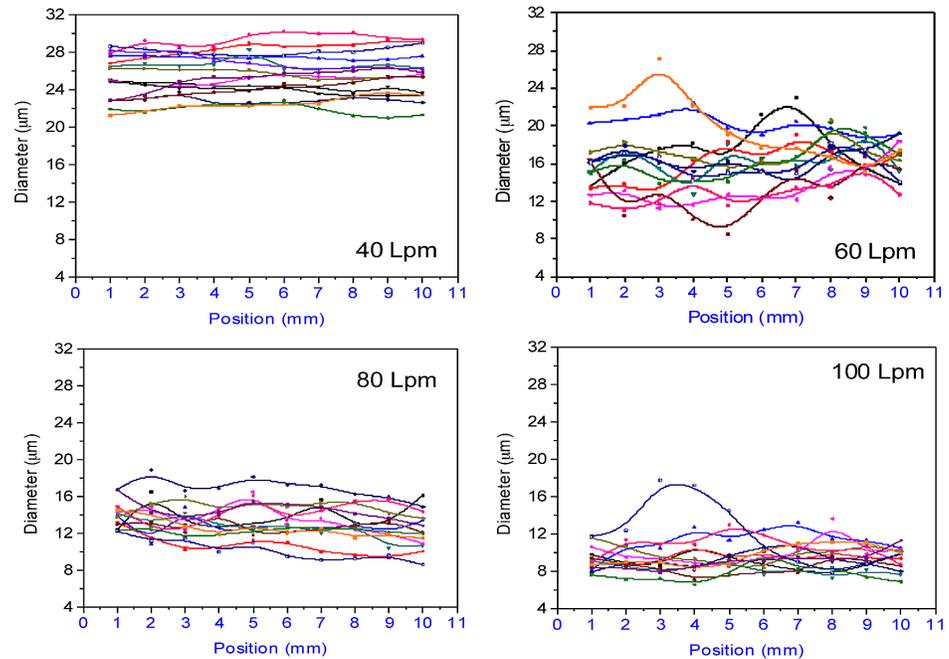
The FDAS765 automatically performs diameter measurements at several longitudinal points, records the elongations, and calculates various parameters related to tensile fracture. Data gathered are transferred to a PC for recording and further analysis.

A typical stress-strain curve (Figure 2-11) has been obtained from a tensile test on a single filament carbon fiber produced at UTSI. This sample was processed at a relatively medium temperature heat treatment at 1050°C. Typically, a nearly linear load-extension relationship is observed after the initially-relaxed fiber sample was fully stretched. Useful data for carbon fiber mechanical properties have been obtained from sufficiently large numbers of single filament tests for statistical analysis.

The fiber diameter variation along the fiber axis and between different fibers was examined with a laser scan micrometer in the fiber length of 10 mm. Figure 2-12 shows the diameter variation comparing four carbon fibers prepared from different pitch fibers spun with blowing speeds at 40, 60, 80, and 100 Lpm, respectively. Obviously, the carbon fibers prepared lacked diameter uniformity along the fiber length and between the different fibers. Fibers spun at 40 Lpm showed less dramatic variation in diameter along the fiber axis as compared to the other fibers spun with faster blowing speeds.

Figure 2-12

Carbon fiber diameter variation along fiber axis and between different fibers



Fiber Surface Modification

Carbon fiber surface treatment is important for producing high-performance composites because it improves fiber surface properties, i.e., surface functional groups and surface area. The increases in surface roughness and reaction points enable more available surface for mechanical, chemical, and physical interlocking and result in a good bonding between carbon fiber and matrix.

Surface Modification by Oxidation

Several surface modification processes, including treatments in air, O_3 [12], CO_2/H_2O [13, 14], and HNO_3 [15, 16] solutions, were evaluated for improving the surface properties of the prepared low-cost carbon fibers. It was considered that gaseous oxidization was suitable for low packing density carbon fiber and economical for low-cost carbon fiber processing. O_3 oxidation at $175^\circ C$ for 60 min is more effective than air, CO_2/H_2O , and HNO_3 oxidation processes. The results from the adsorption of methylene blue [17] and NaOH uptake [18] showed that O_3 oxidation introduces more acidic functional groups and appropriate surface area on the prepared carbon fiber surface [19].

Surface Modification by Sizing

Several nonoxidative CF surface modifications have been reported, including whiskerization, grafting, and coating of different polymers [20]. The coating of polymers could be a simple method of carbon fiber surface modification. In the carbon fiber industry, after the surface treatment, the carbon fibers must

undergo a process called sizing, where the fibers are coated to protect them from damage during winding or weaving. In this effort, a thin layer of epoxy resin was coated with 5 wt% of epoxy/acetone solution on the prepared carbon fibers to increase the surface wettability of the carbon fiber with epoxy resin before the fabrication of CF/epoxy composites.

Interfacial Shear Strength

Typical images of single CF fragmentation tests [21–23] are illustrated in Figure 2-13. Fibers with surface treatments displayed more fragments due to an improved bonding between the fiber surface and epoxy resin. The average fiber fragment length and calculated critical length and interfacial shear strength (IFSS) are listed in Table 2-1. The results show that $\text{CO}_2/\text{H}_2\text{O}$ oxidation at 800°C for 30 min greatly improves IFSS but decreases the fiber tensile strength. O_3 oxidation, without changing fiber tensile strength, leads to a reduced fiber critical length and increased IFSS. Thus, O_3 oxidation proved to be an optimal surface modification process for the prepared CFs.

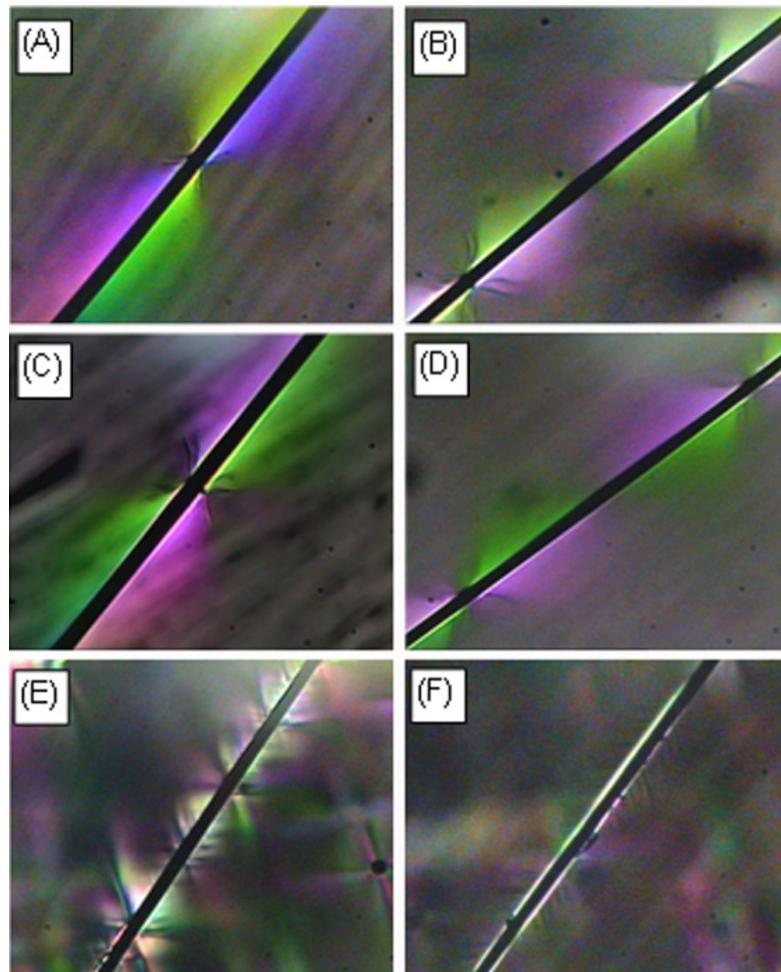


Figure 2-13
 Typical fragmental images of CFs: (A) as-received, (B) O_3 -treated, (C) air-treated, (D) HNO_3 -treated, (E) and (F) $\text{CO}_2/\text{H}_2\text{O}$ -treated CF

Table 2-1

*Fragmentation
Results and
Calculated IFSS*

Fiber Type	Average Length (μm)	Critical Length (μm)	IFSS (Mpa)	Increased IFSS (times)
AS-Received CF	724	965	7.4	1
O ₃ -treated CF	450	600	11.3	1.53
Air-treated CF	711	948	7.6	1.03
CO ₂ /H ₂ O treated CF	<200	<267	>24.8	>3.35
HNO ₃ treated CF	596	795	10.6	1.43

The fragmentation test on sized fiber was compared with as-received fiber by putting two filaments in parallel in a dog-bone mold. The test was carried out under the same conditions for the two filaments. A typical fragmental image is illustrated in Figure 2-14, where the image was taken as a larger strain applied on the dog-bone. More fragments with short fragmental length on the sized CF (top) indicate a strong bonding between fiber surface and epoxy. Fewer fragments with long fragmental length and the appearance of a debonded zone extended from the fiber broken point (bottom) indicate a weak bonding. Table 2-2 lists the measured fragmental length and calculated critical length, comparing sized CF with as-received CF. As expected, small length is presented on the sized CF. Since both fibers have almost the same diameter and tensile strength, the sized CF should have much higher calculated IFSS than the as-received CF. These results suggest that sizing increases wettability of the CF surface, resulting in an improvement in the bonding between the CF surface and matrix.

Figure 2-14

*Fragmental
image comparing
sized CF with as-
received CF*

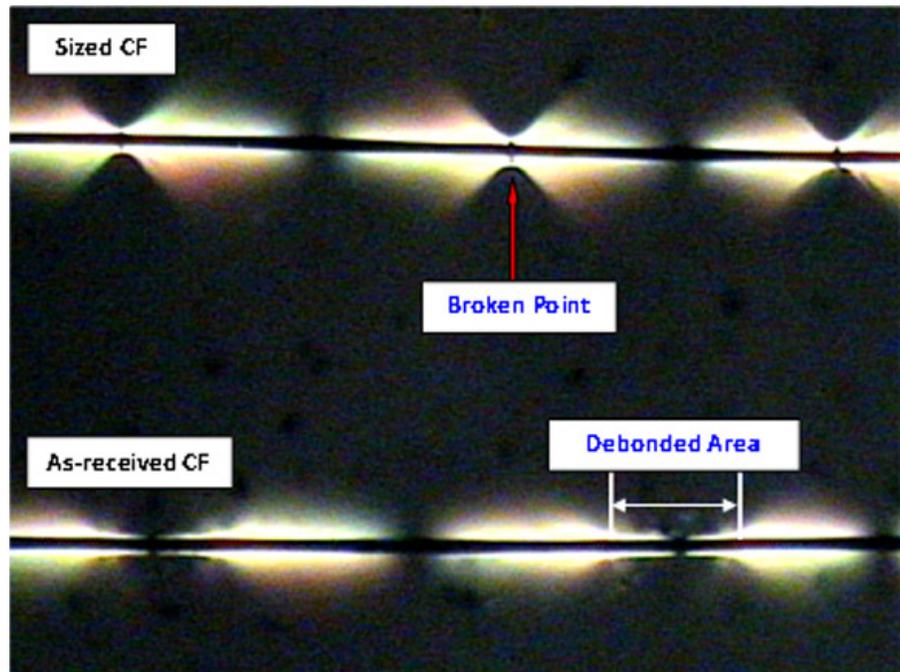


Table 2-2
*Fragmental
Length Results and
Calculated IFSS*

Critical Length	Average Fragmental Length (µm)	Critical Length (µm)
As-received CF	892.9	1190.5
Sized CF	542.3	723.1

SECTION
3

Fabrication and Characterization of Carbon Fiber Composites

The primary purpose of this effort is to assess the potential for a wide range of composite applications of the low-cost carbon fibers produced at UTSI. The composite samples were fabricated using long (continuous) or chopped carbon fibers. The properties of the composites evaluated are strength (tensile, and/or bending), modulus, flexural stiffness, apparent density, and electrical conductivity. The following sections describe the progress made in the experimental fabrications of carbon fibers-reinforced composites.

Forms of Carbon Fibers

Different forms of carbon fibers were prepared in the UTSI Lab [24, 25]:

- **Continuous fibers** – a typical form of carbon fiber produced in the UTSI lab is shown in Figure 3-1. It is continuous long fiber that has many curves and is almost randomly aligned. As compared with commercially available tow fibers, this fiber form has a much lower packing density at $\sim 0.012 \text{ g/cm}^3$. However, it can be aligned with a relatively high degree of fiber orientation for use of composite fabrications.
- **Chopped fibers** – a bundle of carbon fiber was cut to short fiber. The chopped fibers are shown in Figure 3-16 (A) and (B).
- **Fiber rope or tow** – a bundle of carbon fiber was wound to form a rope, as shown in Figure 3-2 (C).
- **Carbon fiber mat** – a bundle of UTSI carbon fiber can easily be fabricated into a carbon fiber mat by using polymers as binders. Several carbon fiber mats have been prepared from continuous or chopped carbon fibers; samples are shown in Figure 3-2 (D)–(G).

Figure 3-1

Typical carbon fiber form—bundle of carbon fibers (continuous fibers)

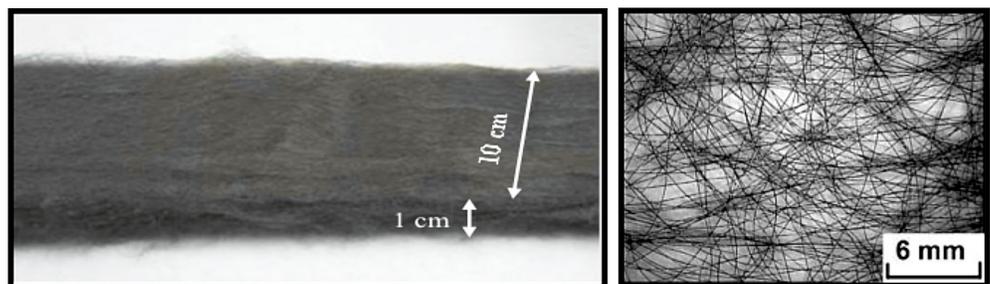
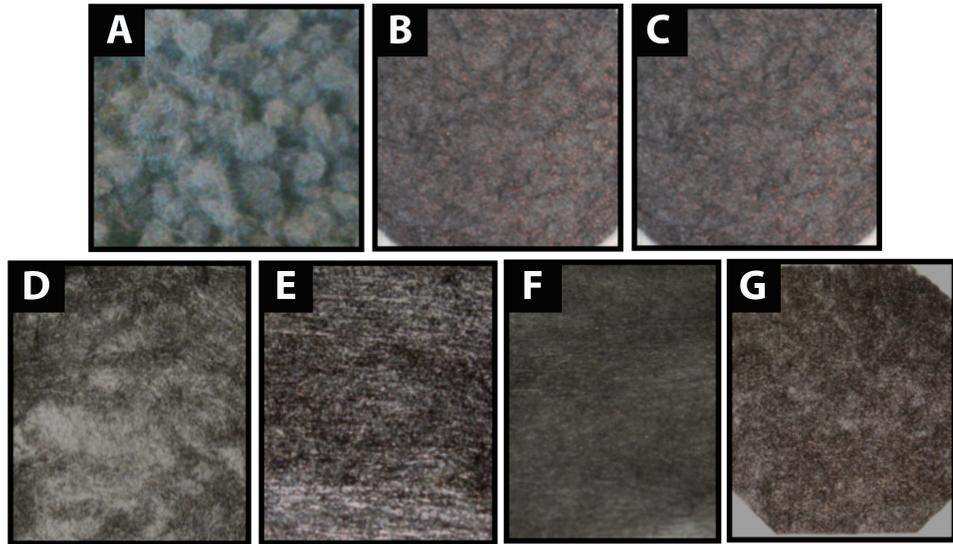


Figure 3-2

Carbon fiber images showing (A) chopped (2-10 mm) fiber, (B) chopped (< 2 mm) fiber, (C) carbon fiber rope, carbon fiber mat made from a bundle of carbon fiber with (D) PVA binder, (E) phenolic resin binder, (F) epoxy binder, (G) chopped carbon fiber (2-10 mm) with phenolic resin binder



Fabrication Techniques

Many different fabrication techniques have been employed at UTSI to produce carbon fiber composites. These include hot compression molding, casting or hand molding with vacuum degassing, vacuum bagging (normal), vacuum bagging resin infusion plus a hot press, and winding. A summary of the used techniques, fiber forms, polymer resins, and composite samples are listed in Table 3-1.

Properties of Some Carbon Fiber Composites

Chopped Carbon Fiber Composites

Prepared carbon fiber can easily be cut into chopped fiber. Chopped fiber composites can be fabricated with epoxy resin using a simple casting or hand-molding technique. The fabricated composites show increased flexural modulus and electrical conductivity with increasing fiber content, as shown in Figure 3-3. However, more pores or air bubbles were found in the composites as the fiber content increased, leading to a decrease in flexural strength.

Figure 3-3

Apparent density, electrical conductivity, and flexural properties of chopped carbon fiber/epoxy composite

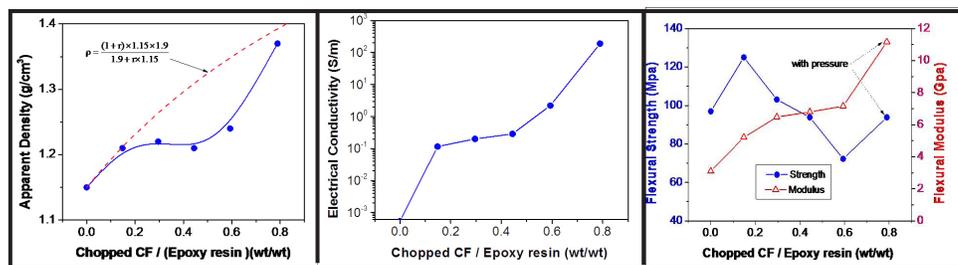
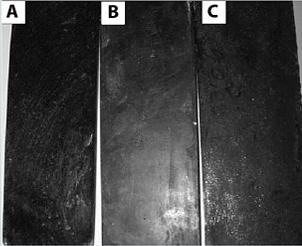


Table 3-1
Fabrication techniques
used for making
UTSI Carbon Fiber
Composites

Fabrication Technique	Fiber Form	Resin	Sample
Hot Compression Molding	(A) Fiber rope (B) Chopped fiber (C) Continuous fiber (random)	Epoxy	
Casting or hand molding (vacuum degassing)	Chopped fiber	Epoxy	
Vacuum bagging (normal)	Continuous fiber	Epoxy	
Vacuum bagging resin infusion plus a hot press	Continuous fiber	Epoxy, Vinylester, Phenolic	
Winding	Continuous fiber	Epoxy	

Continuous Carbon Fiber Composites

To remove air bubbles and increase the mechanical properties of the composites, a vacuum bagging technique and continuous fibers were employed to fabricate composites. However, although air bubbles are reduced by using the vacuum bagging technique, the fiber content usually is less than 20 wt% because the UTSI carbon fiber is much looser and has a very low packing density. Thus, to increase the fiber volume, vacuum bagging resin infusion plus a hot press were used to fabricate the composite. In this case, several layers of carbon fiber were placed between two steel plates (molds), which were then sealed in a vacuum bag. The loosened carbon fiber layers were vacuumed/pressured under a vacuum level at 28" Hg for 30 min. An additional compression was applied by a hot press to increase the

fiber content. The pre-prepared epoxy resin solution (epoxy/hardener= 5/1) was allowed to infuse the fiber layers from one end while keeping the vacuum pump running on the other end.

Fabrication methods and matrix. Table 3-2 lists the physical properties of epoxy/CF composites (CFCs) fabricated with the vacuum bagging (VB) and vacuum bagging resin infusion (VBRI) techniques. The tensile strength, modulus, and E-conductivity increased by adding CF into the epoxy resin. As compared with the VB method (pouring epoxy resin on the layer of CF and then fabricating within vacuum bagging; excess epoxy was absorbed by breath fabric), the VBRI method provides CFCs with higher tensile properties as well as higher apparent density and lower porosity, which was proven by SEM observation. VBRI also provides an ability to control fiber volume/content by applying pressure with a hot press during fabrication. However, the resin infusion time prolonged with increasing pressure [26].

Vinyl ester CFCs were fabricated with the VBRI technique, as listed in Table 3-3. Three phenolic resin CFCs were prepared using three different fabrication conditions, as shown in Table 3-4. A degas process is required to remove solvents in phenolic resin before thermal curing. A high degassing temperature at 150°C leads to fast curing of phenolic resin, which makes the CF lays uncompactible and forms many pores in the composites (showing low density in composite A). Appropriate pressure applied is helpful to increase apparent density and flexural properties of the CFCs.

Both vinyl ester and phenolic resin CFCs present lower mechanical properties than the epoxy CFCs. For all these composites, applied pressure plays a key role for improving their mechanical properties.

Role of fiber compression

By using continuous carbon fiber and vacuum bagging resin infusion plus a hot press technique, the fabricated composites show improved properties (Figure 3-4) over the chopped carbon fiber composites. Carbon fiber content in the composites is increased with applying pressure. As compared with chopped fiber composites (Figure 3-3), the continuous fiber composites display higher electrical conductivity and flexural modulus. However, the apparent density and flexural

Table 3-2
Properties of Epoxy
CFCs Fabricated with
Different Techniques

Property	CFC by VB	CFCs by VBRI	
		Without press	With press
CF content (wt%)	13-18	10-13	26
Density (g/cm ³)	1.13	1.20	1.31
E-conductivity (S/m)	1754	970	3226
Tensile strength (Mpa)	75.9	84.4	124.7
Ultimate strain (%)	0.76	0.92	0.88
Tensile modulus (Gpa)	9.8	8.9	14.6

strength do not increase with applied pressure. Too-high pressure will lead to difficulty for the resin infusion and cause high porosity inside the CFC, which was observed on its polished surface under an optical microscope. It was also found that high pressure leads to carbon fiber crash, which negatively affects the physical properties of the CFCs [26].

Effect of fiber surface modification

Figure 3-5 compares the properties of the composites fabricated with as-received and surface treated CFs. Surface-treated CF composites present higher flexural

Table 3-3

Properties of Cured Vinyl Ester and Its CFCs

Property	CFCs by VBRI	
	Low pressure	High pressure
Apparent density (g/cm ³)	0.97	1.31
E-conductivity (S/m)	2500	1111
Tensile strength (Mpa)	42.3	76.2
Ultimate strain (%)	0.67	0.77
Young's modulus (Gpa)	7.4	10.1

Table 3-4

Properties of Phenolic Resin Composites Fabricated with VBRI

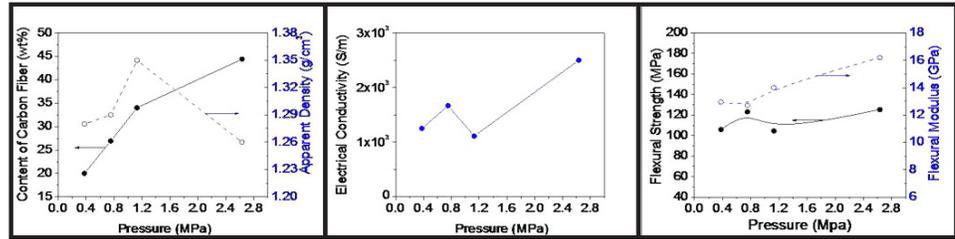
Conditions and Property	A	B	C
Applied pressure (Mpa)	0.3	1.1	2.0
Degas temp. (°C)	150	100	100
CF content (wt %)	37.7	32.3	32.4
Apparent density (g/cm ³)	1000	1000	833
E-conductivity (S/m)	72	105	104
Flexural strength (Mpa)	9.6	14.4	14.9

strength and modulus and lower E-conductivity than the as-received CF composite. O₃-treated CF is better than HNO₃-treated CF for making high performance CF composites [19]. Increases of 72 percent and 30 percent in flexural strength and modulus are obtained by the O₃ oxidized fiber/epoxy composite.

A comparative study was conducted to investigate the effect sizing with 5 wt% of epoxy solution on the mechanical properties of the CF composites, as shown in Table 3-5. It was found that resin infusion is faster in the sized fiber than in the as-received fiber. The content of carbon fiber in the composites is 28–30 wt%. The increase in wettability of the sized CF surface results in a good bonding and an improvement in mechanical properties of the CFCs [19]. Increases of 52 percent and 28 percent in flexural strength and modulus are obtained by sized fiber/epoxy composite.

Figure 3-4

Effect of applied pressure on fiber content, apparent density, electrical conductivity, and flexural properties of continuous carbon fiber / epoxy composites



Hybrid Composites

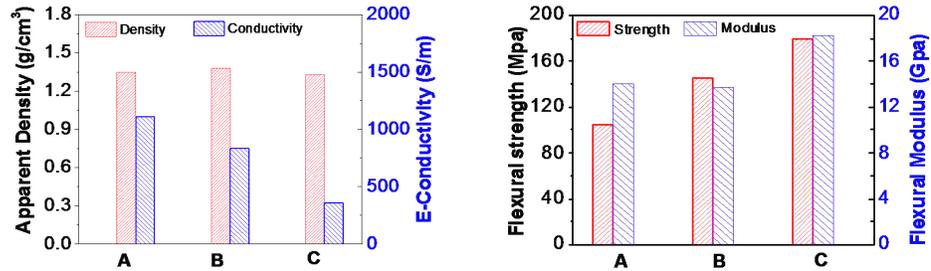
Hybrid composites were fabricated with two different reinforcing materials: UTSl carbon fibers and commercially-available PAN-based carbon fiber or low-cost calcined coke fines.

UTSl carbon fiber with PAN-based carbon fiber

Lightweight, cost-effective hybrid sandwiched composites (Figure 3-6) were prepared using two kinds of carbon fibers: low-cost and relatively lower performance UTSl carbon fiber, used as core materials; and commercially-available PAN-based carbon fiber (fabric) with high-cost and higher performance, used as skin materials.

Figure 3-5

Effect of fiber surface modification on properties of the composites: (A) as-received CF, (B) HNO₃-treated CF, (C) O₃-treated CF



The hybrid (sandwiched) composites with a solid core display not only simplified the fabrication process but also improved properties, such as higher e-conductivity, lower apparent density, and good flexural strength and modulus, as shown in Table 3-6. The hybrid (sandwiched) composites with a porous core show much lower density than 1 g/cm₃ as well as high e-conductivity, as shown in Table 3-7. Both solid core and porous core hybrid (sandwiched) composites present great improvements in flexural stiffness due to an increased thickness, as shown in Table 3-8. These lightweight hybrid composites may have other unusual advantages, such as low and uniform thermal expansion behavior and high thermal stability, over conventional sandwich composites [27].

Table 3-5

Effect of Sizing on Properties of CFCs

CFC	Apparent Density (g/cm ₃)	E-Conductivity (S/m)	Flexural Strength (Mpa)	Flexural Modulus (Gpa)
Un-sized CF	1.313	2000	104	14.0
Sized CF	1.352	1961	158	17.9

UTSI carbon fiber with calcined coke fines

UTSI chopped carbon fiber was mixed with powder materials (calcined coke fines) to reinforce epoxy resin to form hybrid composites. Figure 3-7 compares seven hybrid composites (bar) with powder/epoxy composites (line). UTSI chopped carbon fiber is more effective than calcined coke fines in promoting electrical conductivity and flexural modulus of the composites. Hybrid composites not only take advantage of low-cost calcined coke fines but also improve the electrical conductivity and modulus of the composites by the addition of a small amount of chopped carbon fiber.



Figure 3-6

Hybrid (sandwiched) composites fabricated with UTSI CF (core) and PAN-CF fabric

Table 3-6

Properties of Hybrid Composites with Solid Core Made from UTSI CFCs

Composites	Thickness (mm)	E-conductivity (S/m)	Density (g/cm ³)	Flexural property	
				Strength (Mpa)	Modulus (Gpa)
S0: no core	~1.1	1667	1.55	637	60
S1	~2.1	2000	1.51	500	70
S2	~2.8	3333	1.40	430	49

Table 3-7

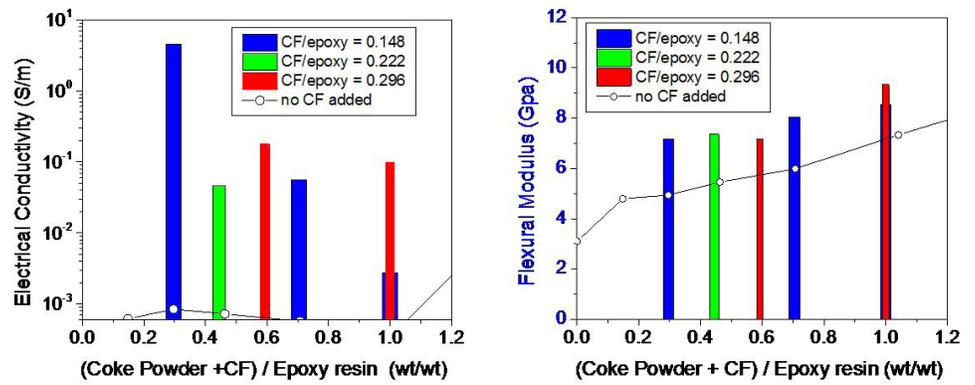
Properties of Hybrid Composites with Porous Core Made from UTSI CFCs

Composites	Thickness (mm)	Density (g/cm ³)	E-conductivity (S/m)
P1	2.32	1.30	5000
P2	2.83	1.16	5000
P3	3.83	0.88	2500
P4	7.10	0.57	1429

Table 3-8
 Flexural Stiffness of
 Hybrid Composites;
 Cores Made from
 UTSI CFCs

Composites	Thickness (mm)	Flexural Stiffness		
		N-m ²	Std. Dev.	Increase (times)
S0	1.10	0.047	0.0063	1
S1	2.03	0.483	0.056	10.3
S2	2.87	0.946	0.167	20.1
P1	2.32	0.754	0.086	16.0
P2	2.83	0.975	0.052	20.7
P3	3.83	1.907	1.075	40.6
P3	7.10	1.546	1.807	32.9

Figure 3-7
 Effect of added CF
 on properties of hybrid
 composites



Conclusions and Recommendations

A fiber spin lab has been set up using components donated to UTSI by ConocoPhillips. Pitch-based carbon fibers have been successfully produced, thermally treated, and mechanically characterized. Various composites have also been made and evaluated. Under this FTA program, significant progress has been made in the continued development and refinement of low-cost carbon fiber production and composite application technologies. The properties of the fibers produced and evaluated compare well with the pitch-based fibers that are commercially available. More specifically, the following conclusions and recommendations can be made based on our current work.

1. Pitch-based, low-cost carbon fiber production technologies have been reproduced in the UTSI laboratory, with fiber spinning throughput around 1 pound/hour achieved.
2. The pitch fibers have been successfully processed into carbon fibers with high mechanical strength and modulus. However, thermal processing has been relatively slow because of the batch processing method, relatively slow drying and stabilization processes, and low packing density of green fiber materials. Better processing methods and equipment need to be developed to accommodate the current green fiber production rate.
3. A final heat treatment temperature currently at 1500°C produced a small amount of carbon fibers with good mechanical properties. To produce carbon fibers with higher modulus and excellent thermal and electrical conductivity for multifunctional materials, higher temperature (> 2200 °C) treatment or graphitization systems are required and are recommended to be investigated further in the next phase.
4. Pitch fibers with diameters below 10 microns have been spun and demonstrated, indicating potential for further improvements in carbon fiber properties.
5. Preliminary experiments have indicated that partial alignment of fibers can be achieved at the laydown stage during bowing spin. The composite samples made from the partially-aligned carbon fibers have confirmed the anisotropy of fiber reinforcement.
6. Varied forms of carbon fiber-reinforced polymer (CFRP) composites have been successfully produced in the lab using several fabrication techniques, indicating great potential of the CFRP composites for low-cost applications in automobiles, public transit vehicles, concrete reinforcements, and many other areas.
7. The carbon fibers produced in the UTSI lab have significantly increased the strength and modulus of the CFRP composites. However, much

higher mechanical properties could be attained if the carbon fiber volume was increased and fiber alignment and fiber-matrix bonding were further improved.

8. Fiber surface treatment with oxidation and sizing indicated that oxidation with O_3 and sizing with a thin layer of epoxy can effectively improve fiber surface properties, including oxygen-containing acidic functional groups and/or surface area, and can result in a distinct increase in the mechanical properties of the CF/epoxy composites.
9. The fiber alignment and low packing density of the fiber are apparently two major bottlenecks that have impacted the properties of the composites that are produced from our low-cost carbon fibers. It is recommended that these areas be vigorously investigated in the next phase.

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